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THE ELECTROWINNING OF COPPER ARSENIDE

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THE ELECTROWINNING OF COPPER ARSENIDE

by

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ABSTRACT

Copper arsenide deposits containing up to 40% arsenic were electrowon from simulated copper refinery secondary liberator cell electrolyte. The arsenic content increased with increasing current density and decreasing Cu/As ratio in the electrolyte. Polarization studies indicated that copper arsenide deposition occurred at potentials cathodic to +0.12 V vs NHE and that arsine evolution did not occur until a cathodic potential of -0.36 V vs NHE was attained. The deposits were coarse and dendritic; they consisted of a thin layer of copper over which a layer of copper arsenide was deposited. Electron microprobe analysis indicated that the copper arsenide formed was $Cu_{3-x}As$.

Keywords: Electrowinning, Copper arsenide, Electrorefining, Deposition of copper arsenide, Arsine formation.

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ÉLECTRO EXTRACTION DE L'ARSÉNIATE DE CUIVRE

par

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RÉSUMÉ

Des dépôts d'arséniate de cuivre contenant jusqu'à 40 % d'arsenic ont été extraits par électrolyse d'une cellule d'électrolyse secondaire au cours d'un affinage simulé. La teneur en arsenic a augmenté en fonction de l'augmentation de la densité du courant et diminué le rapport Cu/As dans l'électrolyte. Des études de polarisation démontrent que les précipitations d'arséniures de cuivre se sont produites à des potentiels cathodiques atteignant jusqu'à +0,12 V vs NHE et que l'évolution de l'arsine ne s'est produite que lorsqu'un potentiel cathodique de -0,36 V vs NHE a été atteint. Les dépôts étaient granuleux et dendritiques et consistaient en une fine couche de cuivre sur laquelle un couche d'arséniate de cuivre s'était déposée. Une analyse colorimétrique a démontré que la formation d'arséniate de cuivre était constituée de $Cu_{3-x}As$.

Mots-clé: Électro extraction, arséniate de cuivre, électroraffinage, dépôts d'arséniate de cuivre, formation d'arsine.

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INTRODUCTION

The presence of arsenic in anode copper can result in better cathode purity during copper electrorefining because arsenic promotes increased slime stability and adherence. As a result, there are fewer suspended solids and, therefore, less chance of their inclusion as impurities in the cathode. Arsenic also counteracts the anode passivation effects of other trace elements such as antimony (1). High-arsenic copper, however, usually leads to the build-up of high soluble arsenic concentrations in the electrolyte that enhances the possibility of arsine gas generation in the liberator cells. It appears that there is a minimum level of arsenic in the anodes which is desirable and this is dependent on the level of other impurities present in the anode.

One means of increasing the arsenic content of anode copper when insufficient arsenic is present is to dope the copper melt with arsenic prior to anode casting. Since arsenic trioxide, the most readily available form of arsenic, is volatile, copper-arsenic alloys probably would be required for doping purposes. The presently available copper arsenides are either pure and expensive since they are prepared by thermal synthesis from the constituent elements or impure lead blast furnace speiss products. As neither feed may be desirable, it may be necessary to use a copper arsenide + copper mixture obtained as an electrodeposit from copper electrolyte containing dissolved arsenic. Soluble arsenic present in copper electrolyte exists for the most part as arsenic(V) (2), and is not

reduced to metallic arsenic or copper arsenic compounds during the liberation operation (3). The addition of arsenic(III) to a copper refinery secondary liberator cell electrolyte, however, seems to produce copper arsenides at the cathode that are suitable for doping the cast anodes with arsenic.

Prior to starting the current experimental program, a detailed survey was made of the available literature on the electrodeposition of copper-arsenic alloys. The results of the literature review, including arsenic electrochemistry, have been reported elsewhere (4). A significant reference in the literature survey was the work of Dewalens et al. (3) who studied many aspects of the electrodeposition of copper-arsenic alloys. They found that arsenic did not deposit near its reversible potential on platinum in 500 g/L H_2SO_4 medium. In the presence of Cu^{2+}, however, copper arsenide deposits at potentials cathodic to +0.200 V vs NHE. There was no evidence for the deposition of metallic arsenic.

Japanese workers have patented a process for removing copper and arsenic from copper electrolyte (5). The decoppered electrolyte from a copper sulphate plant (6) associated with a copper electrorefining operation was electrolyzed to give copper arsenic products. The soluble arsenic existed mainly in the +5 state and had to be reduced to the +3 state before the electrolysis was successful. The method used for As(V) reduction was not specified but chemical reactions were

recommended. The patent disclosure indicated that during the electrolysis of As(V)-containing solutions, the copper concentration decreased from >13 g/L to <1 g/L whereas the arsenic concentration decreased from 12.5 g/L to 6 g/L. Continued electrolysis resulted in cathode polarization and arsine gas generation.

With regard to the composition of the copper-arsenic electrodeposits, Dewalens et al. (3) found that there did not appear to be a sharp boundary between the formation conditions for the different Cu-As phases. The alloys formed at the limiting current density for high relative arsenic concentrations were $Cu_{5-x}As_2$ in mixtures with some Cu_2As, β-$Cu_{3-x}As$ or $\alpha Cu_{3-x}As$. Below the limiting current at high relative arsenic concentrations, β-$Cu_{3-x}As$ was obtained. At high relative copper concentrations, the copper-rich phases, β-$Cu_{3-x}As$, α-$Cu_{3-x}As$, ε phase, and α copper were identified by XRD.

The Japanese workers (5), using constant potential electrolysis techniques, found that the electrodeposits consisted mainly of Cu_2As and $Cu_{3-x}As$ for solutions containing As(III), and mainly Cu metal and some Cu_2As for solutions containing As(V).

In the present study the effects of electrolyte composition, current density and electrolyte circulation rate on the electrowinning of copper arsenide from simulated liberator cell electrolyte were determined. The electrodeposits were characterized using SEM, EDXA and electron microprobe techniques.

EXPERIMENTAL

Copper arsenide deposits were electrowon at various current densities at 65°C using both batch and continuous feed electrolysis procedures. Batch electrolysis was done using three different electrolyte compositions, Table 1, having initial Cu/As ratios of 0.5, 1.0 and 2.0. For the continuous feed electrolysis, the feed electrolyte had an Cu/As ratio of 2.5 whereas the cell electrolyte had an initial Cu/As ratio of 2.0, Table 1. All electrolytes contained 200 g/L H_2SO_4. The electrolytes were prepared from reagent grade $CuSO_4.5H_2O$, As_2O_3 and H_2SO_4.

The experimental set-up for batch electrowinning of copper arsenides is shown in Figure 1. It consisted of an electrolysis cell, an electrolyte circulation vessel and a detector for arsine. The electrowinning cell was a 250 mL tempering beaker with a tight-fitting cover made from 18 mm plexiglass. Holes were drilled in the cover to hold and space the electrodes and to accommodate the electrolyte inlet and outlet tubes. Electrolyte was circulated, usually at a rate of 2 mL/min, by pumping from the circulation vessel into the cell and from the cell back into the circulation vessel. The outlet tube from the cell was fixed at a level such that the cell volume was maintained constant at 200 mL.

The cathode was a Ti sheet; copper arsenide was deposited on both sides over a total area of 14.8 cm^2. The edges of the Ti sheet were masked using edge strips to facilitate stripping of the deposit. Two Pb-Sb anodes were used, one on either side of the cathode. The cathode potential was monitored during electrolysis by using a mercury/mercurous sulphate (MSE) reference electrode.

Arsine evolution at the cathode was detected by using a solution containing 0.2% silver diethyldithiocarbamate in pyridine. This solution changes colour from yellow to deep red in the presence of trace arsine. Any arsine evolved at the cathode would be returned to the circulation vessel with the return electrolyte. The filtering flask which served as the circulation vessel (Figure 1) was sealed at the top so that any arsine entering the circulation vessel would exit via the side arm which lead directly into the solution in the detector flask.

For the 6-h electrowinning experiments, 1-L of the desired test solution (Table 1) was prepared. 200 mL of this solution was placed in the cell, 700 mL in the circulation vessel and the remaining 100 mL was retained for analysis to determine the initial concentrations of Cu^{2+} and As(III). The cell solution was heated to and maintained at 65°C by circulating hot water between the walls of the electrolysis cell using a circulating water bath. For the 12-h electrowinning tests, a 2-L volume of the desired test solution was prepared; 200 mL for the cell, 1700 mL for the circulation vessel and 100 mL for analysis. At the end of the tests, the cathode was removed from the cell and rinsed with water. The deposit was stripped from the Ti blank and allowed to dry overnight prior to weighing. The cell electrolyte and solution in the circulating vessel were combined and the total volume was recorded. A sample was taken for analysis to determine the final concentrations of Cu^{2+}, total arsenic and in some cases As(V) (2).

The experimental set-up for the continuous feed electrowinning of copper arsenide is shown schematically in Figure 2. The electrowinning cell was the same one used for the batch electrolysis. The feed electrolyte was pumped into the cell at a rate which maintained a constant concentration of Cu^{2+} in the cell. The solution volume in the cell was maintained at 200 mL by pumping the spent electrolyte into a collection flask. The arsine detector in this case was placed after the spent electrolyte receiver, Figure 2. The compositions of the feed and cell electrolytes used in these tests are given in Table 1.

The polarization behaviour of copper arsenide deposition also was determined using potentiodynamic techniques. These studies were done in the same cell used for the electrodeposition studies that contained 200 mL of the desired electrolyte. The cathodic polarization curves were obtained using a PAR model 173 potentiostat in conjunction with a PAR model 175 universal programmer and a X-Y recorder.

Chemical analysis of solutions and deposits was done using atomic absorption spectrophotometry. The morphology, structural characteristics and composition of the arsenide phases were determined by using SEM, EDXA and electron microprobe techniques (7).

RESULTS AND DISCUSSION

POLARIZATION STUDIES

i) Potentiodynamic Measurements

Potentiodynamic cathodic polarization (i vs E) curves were obtained for each electrolyte composition. Starting from the rest potential, the potential was increased in the cathodic direction at a rate of 20 mV/s. Figure 3 shows a series of i vs E plots obtained for solutions having initial Cu/As ratios of 0.5, 1.0 and 2.0. The curves are characterized by two peaks; the first peak occurs at +0.18 V vs NHE and is independent of the Cu/As ratio. This peak represents a maximum for copper deposition, and copper arsenide is not deposited in this potential region. Co-deposition of copper arsenide begins at about +0.12 V vs NHE; i.e., at the beginning of the second peak. This potential (+0.12 V vs NHE) is also independent of the Cu/As ratio in the electrolyte. The maximum of the second peak, however, occurs at more cathodic potentials with an increase in the Cu/As ratio. Similar polarization curves were reported by Dewalens et al. (3); however, their curves were characterized by plateaus rather than peaks probably because the scan rate employed was only 0.6 mV/s.

Under the experimental conditions used in this work, arsine evolution was not detected until the cathode potential reached a value of $\sim$-0.36 V vs NHE. The plateau regions in the curves of Figure 3 that occur at -0.23 V vs NHE are probably the prelude to arsine and hydrogen co-evolution.

ii) Chronopotentiometric Measurements

Copper arsenide deposits were obtained at constant current density for each electrolyte composition and the cathode potential was recorded as a function of time. Strong potential oscillations occurred particularly in the potential region of the second wave, Figure 3. Examples of these potential oscillations, also noted by Dewalens et al. (3), are shown in Figures 4(a) and 4(b). Figure 4(a) shows the 2.5-3.0 hour segment of a potential-time profile obtained during the 6-hour deposition of copper arsenide at 40 A/ft^2, whereas Figure 4(b) shows the 4.5-5.0 hour segment of another potential-time profile obtained under similar experimental conditions.

Chemical analysis of the deposits indicates that the arsenic content increases as the potential becomes more cathodic; i.e., more negative. Optical microscopic examination of deposit cross-sections indicated a layered structure; i.e., a layer of copper, followed by a layer of copper arsenide followed by another layer of copper and so on. Thus, it appears that at the low cathodic potential the deposit consists mainly of copper whereas when the potential rises to more cathodic values, a copper arsenide layer is deposited. The deposit composition and structure will be discussed in detail in a later section of this report.

Figure 4(b) shows a potential excursion to a high cathodic value ($\sim$-0.36 V vs NHE) during the latter stages of deposition. When the cathode potential reached this value, arsine evolution was detected. Arsine formation was not detected as long as the cathode potential remained less cathodic than -0.36 V vs NHE.

COPPER ARSENIDE DEPOSITION

i) Constant Current Bulk Electrolysis

Copper arsenide deposits were electrowon from each electrolyte composition at various current densities for periods of 3.5 to 12 hours. The effects of current density, electrolyte circulation rate and the initial Cu/As ratio of the electrolyte on the arsenic content of the deposits were determined. The results obtained from batch electrolysis using electrolytes having initial Cu/As ratios of 0.5, 1.0 and 2.0 are summarized in Table 2. At an initial Cu/As = 0.5, the arsenic content of of the deposit increased with increasing current density, Figure 5. As expected, the current efficiency for copper deposition decreased and that for arsenic deposition increased with increasing current density corresponding to the increase in the arsenic content of the deposit. The combined current efficiency was >94%, Table 2.

At a constant current density of 30 A/ft^2 (323 A/m^2), the arsenic content of the deposit decreased with an increase in the initial Cu/As ratio in the electrolyte, Figure 6.

The arsenic content of the deposits (Table 2) was determined by dissolving a known weight of the product in nitric acid, diluting to a known volume and analysing for total arsenic using atomic absorption spectrophotometry. The arsenic content of the deposits was also calculated using the solution analyses. The amount of metal deposited was calculated from the differences between the initial and final copper and arsenic concentrations in the electrolyte, Table 3. As indicated in Table 3, there is reasonable agreement between the measured and calculated

deposit weights. The agreement between the calculated and analyzed arsenic contents of the deposit varies between 0.7 and 8.2%, Table 3.

For the 11 and 12 h deposits, Table 2, the As(V) concentration in the final electrolyte was determined. In both cases, 45% of the total arsenic remaining in solution after electrolysis was in the +5 state. According to the results of Dewalens et al. (3) and Terasaki et al. (6), As(V) does not form arsenide but rather increases the probability of arsine generation.

ii) Constant Current Continuous Feed Electrolysis

The effect of current density and feed rate on the arsenic content of deposits electrowon from a cell electrolyte containing 8 g/L Cu^{2+} + 4 g/L As(III) + 200 g/L H_2SO_4 (Cu/As = 2.0) and a feed electrolyte containing 25 g/L Cu^{2+} + 10 g/L As(III) + 200 g/L H_2SO_4 (Cu/As = 2.5) was determined at 65°C. The results are summarized in Table 4. At 40 A/ft^2 (430 A/m^2) current density, the arsenic content of the deposit decreased with an increase in the feed rate. An increase in feed rate decreases the cathode polarization and this favours copper rather than copper arsenide deposition.

In general, the arsenic content of the deposits also decreases with decreasing current density (Table 4) as noted earlier for the batch electrolyses (Table 2). For the tests done at the different current densities, the feed rate was also adjusted in an attempt to maintain a constant copper concentration in the cell electrolyte.

iii) Constant Potential Bulk Electrolysis

As indicated by the polarization curves, Figure 3, copper arsenide deposition occurred for potentials cathodic to +0.12 V vs NHE. In view of this, two deposits were obtained under controlled potential electrolysis at 0.00 V and -0.100 V vs NHE for 6 hours. During the controlled potential electrolysis, the cathodic current was recorded as a function of time. The electrolyte used had an initial Cu/As = 2.0; i.e., electrolyte (c) in Table 1. At constant potential electrolysis, the current was observed to oscillate with time, similar to the potential oscillations noted during constant current electrolysis, Figures 4(a), (b). Figure 7 presents plots of the average current vs time for each of the controlled potential electrowinning tests. As expected, the electrolysis done at the more cathodic potential; i.e., -0.100 V vs NHE, exhibited the higher current and as a result the deposit contained more arsenic. The arsenic content of the deposit electrowon at -0.100 V vs NHE was 8.2% whereas that of the deposit electrowon at 0.00 V vs NHE was 1.9%.

CHARACTERIZATION OF COPPER ARSENIDE DEPOSITS

The copper arsenide deposits were generally smooth and copper coloured on the side in contact with the Ti cathode and reddish-grey and dendritic on the solution side. The SEM micrograph, Figure 8, shows the dendritic surface of the deposit. The surface is characterized by clusters of grains growing out of relief from the initial deposit. These grains are almost completely black with a few copper-

coloured highlights. Qualitative EDXA showed that arsenic occurs along the surface of most grains. In polished section, the copper grains were found to have a discontinuous layer of copper arsenide.

Sections of the copper arsenide products were mounted and polished in cross section so that the sequence of deposition and identification of the phases could be determined. As shown in Figure 9, the deposit is composed of a thin copper plate covered by a carpet of copper dendrites of different heights. The copper plate and the lower portions of the dendrites are covered with an almost continuous layer of a copper arsenide (bright) of variable thickness, Figure 10. A very thin deposit of the arsenide also was flashed onto the copper dendrites. This is clearly indicated in the As Kα X-ray micrograph, Figure 11, where the concentration of white dots defines the arsenide phase.

A minor third phase occurs as a thin discontinuous layer sandwiched between the copper plate and the copper arsenide layer, and as scattered crystals over the surface of the dendrites, Figure 10. Electron microprobe analysis of the few large crystals (10 μm) tentatively identified this phase as Cu_2O containing a small amount of arsenic.

The electron microprobe analyses of the copper arsenide phases of a number of deposits obtained at various current densities are summarized in Table 5, and the data clearly indicate that the arsenide phase is $Cu_{3-x}As$.

CONCLUSIONS

The electrowinning of copper arsenide has been studied using both batch and constant feed electrolysis techniques. Batch electrolysis was done using electrolytes containing initial Cu/As ratios of 0.5, 1.0 and 2.0. At constant current density, the arsenic content of the deposits decreased with increasing initial Cu/As ratio. For a given Cu/As ratio, the arsenic content of the deposit increased with increasing current density. In addition, some of the initially present As(III) was oxidized at the anodes to As(V), and as such, was not available for deposition at the cathode. The results obtained from the continuous feed electrolysis tests were essentially the same as those obtained from batch electrolysis.

Measured polarization curves indicated that copper arsenide deposition occurred for potentials cathodic to +0.12 V vs NHE. This was confirmed by controlled potential electrolysis tests done at 0.00 V and -0.100 V NHE. Potential oscillations that occurred during constant current electrolysis (and current oscillation occurred during controlled potential electrolysis) may be related to the layered structure of the deposit. Arsine generation was not observed until a cathodic potential of $\sim$-0.36 V vs NHE was attained.

The surface of the copper arsenide deposits consisted of clusters of grains growing out of relief from the initial deposit layer; i.e., the deposits were dendritic. EDX analysis of polished cross sections of selected deposits showed that the initial copper deposit as well as the bottom portions

of the copper dendrites are covered with an almost continuous layer of copper arsenide of variable thickness. Electron microprobe analysis of the copper arsenide phase showed it to be $Cu_{3-x}As$.

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Table 1. Summary of Electrolyte Compositions

Electrolysis (Type)	Electrolyte Composition	Initial Cu/As (Cell)	Initial Cu/As (Feed)
a) Batch	4 g/L Cu^{2+} + 8 g/L As(III) + 200 g/L H_2SO_4	0.5	-
b) Batch	8 g/L Cu^{2+} + 8 g/L As(III) + 200 g/L H_2SO_4	1.0	-
c) Batch	8 g/L Cu^{2+} + 4 g/L As(III) + 200 g/L H_2SO_4	2.0	-
Continuous Feed	25 g/L Cu^{2+} + 10 g/L As(III) + 200 g/L H_2SO_4	-	2.5
Continuous Cell	8 g/L Cu^{2+} + 4g/L As(III) + 200 g/L H_2SO_4	2.0	-

Table 2. Effect of Initial Cu/As Ratio and Current Density on the Composition of the Deposits and on the Current Efficiency for Deposition Obtained for Batch Electrowinning of Copper Arsenide

Cu/As (Ratio) Initial	CD* (A/ft^2)	Time (H)	As (%)	CE (%)		
				Cu	As	Cu+As
0.5	20	7.0	20.1	72.5	23.2	95.7
0.5	30	6.5	29.7	61.4	33.0	94.4
0.5	40	3.5	46.1	47.1	51.2	98.3
1.0	30	7.0	9.4	89.0	11.8	100.8
2.0	30	7.0	3.0	94.9	3.7	98.6
2.0	40	5.0	12.8	83.7	15.7	99.4
2.0	30	11.0	2.4	95.5	3.0	98.5
2.0	40	12.0	13.4	80.2	15.8	96.0

65°C; Circulation rate = 2 mL/min

*1 A/ft^2 = 10.76 A/m^2

Table 3. Mass Balances Obtained for Batch Electrowinning of Copper Arsenide at 65°C

Cu_i (g)	Cu_f (g)	$Cu° = (Cu_i - Cu_f)$ (g)	As_i (g)	As_f (g)	$As° = (As_i - As_f)$ (g)	$Cu° + As°$ (g)	Cathode (g)	Percent As	
								(Calculated)	(Analysis)
16.95	8.68	8.27	8.04	6.88	1.16	9.43	9.4764	12.3%	(13.4%)
15.83	9.28	6.55	8.25	8.00	0.25	6.75	6.7100	3.7%	(2.4%)
7.50	3.36	4.14	3.70	3.42	0.28	4.42	4.4909	6.3%	(8.2%)
7.72	3.72	4.00	3.65	3.49	0.16	4.16	4.2688	3.9%	(3.0%)
3.74	2.14	1.60	7.29	6.39	0.98	2.58	2.5365	37.9%	(46.1%)

Table 4. Effect of Initial Cu/As Ratio and Current Density on the Composition of the Deposits and the Current Efficiency for Deposition Obtained for Continuous Feed Electrowinning of Copper Arsenide at 65°C

Cu/As (Feed)	Initial Cu/As (Cell)	CD (A/ft^2)*	Feed Rate (mL/min)	Time (H)	As (%)	CE (%)		
						Cu	As	Cu+As
2.5	2.0	40	0.68	6.0	1.6	97.1	2.0	99.1
2.5	2.0	40	0.49	5.8	11.4	87.4	14.3	101.7
2.5	2.0	40	0.45	5.5	17.0	98.0	20.3	98.3
2.5	2.0	35	0.40	6.0	6.6	89.0	8.0	97.0
2.5	2.0	30	0.32	6.5	3.4	92.7	4.2	96.9
2.5	2.0	20	0.20	6.8	0.3	98.3	0.4	98.7

Feed Electrolyte: 25 g/L Cu^{2+} + 10 g/L As(III) + 200 g/L H_2SO_4

Cell Electrolyte: 8 g/L Cu^{2+} + 4 g/L As(III) + 200 g/L H_2SO_4

*1 A/ft^2 = 10.76 A/m^2

Table 5. Electron Microprobe Analysis of the Arsenides

Current Density (A/ft^2)*	Time (h)	Av. Wt.% Cu	Av. Wt.% As	Total	Computed Formula (Cu_xAs)
20	6.75	71.0	29.4	100.4	$Cu_{2.9}As$
30	6.50	69.4	31.3	100.7	$Cu_{2.6}As$
30	11.0	71.6	28.0	99.6	$Cu_{3.0}As$
35	6.0	69.8	30.6	100.2	$Cu_{2.7}As$
40	5.75	70.5	29.8	100.3	$Cu_{2.8}As$
40	5.50	70.0	29.4	99.4	$Cu_{2.8}As$
40	5.0	69.7	30.6	100.3	$Cu_{2.7}As$

*1 A/ft^2 = 10.76 A/m^2

FIGURE CAPTIONS

Fig. 1 - Experimental set-up for batch electrowinning of copper arsenide.

Fig. 2 - Experimental set-up for continuous feed electrowinning of copper arsenide.

Fig. 3 - Potentiodynamic i-E curves obtained for electrolytes (a), (b) and (c), Table 1, at 20 mV/s and 65°C.

Fig. 4 - Potential-time segments obtained at 40 A/ft^2 (430 A/m^2) for copper arsenide deposition from electrolyte (c), Table 1, at 65°C with circulation rate = 2 mL/min. a) 2.5 - 3.0 h segment; b) 4.5 - 5.0 h segment.

Fig. 5 - Plot of percent arsenic in the deposit vs current density obtained for an initial electrolyte with Cu/As - 0.5 at 65°C and circulation rate = 2 mL/min (1 A/ft^2 = 10.76 A/m^2).

Fig. 6 - Plot of percent arsenic in the deposit vs Cu/As ratio obtained at 30 A/ft^2 (323 A/m^2), 65°C and circulation rate = 2 mL/min.

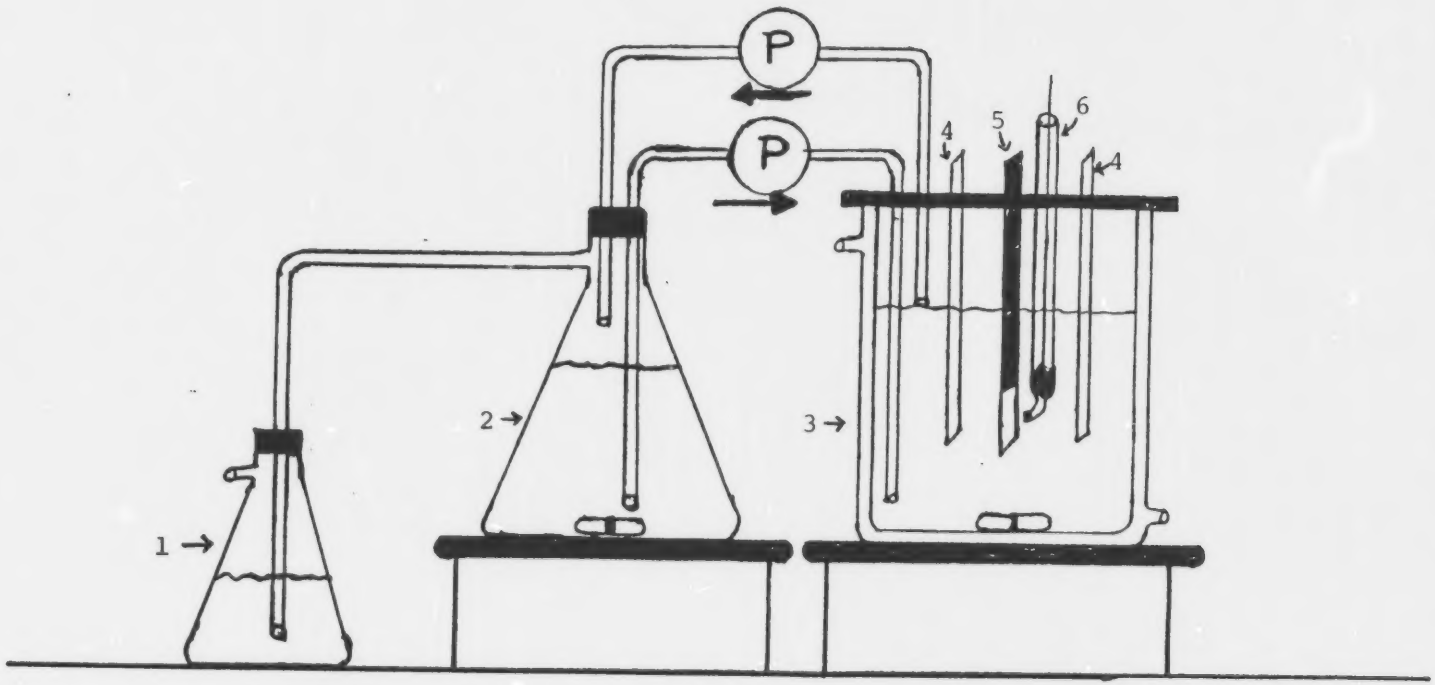
Fig. 7 - Cathodic current vs time plots for copper arsenide deposition under controlled potential electrolysis at 0.00 V and -0.100 V vs NHE using solution (c), Table 1 at 65°C.

Fig. 8 - Scanning electron micrograph showing the surface of the copper arsenide deposit electrowon at 20 A/ft^2 (215 A/m^2).

Fig. 9. - Backscattered electron micrograph of a polished section prepared from a copper arsenide deposit showing the height and size of the copper dendrites (medium grey). The white layer on the copper plate and thin coating on the lower portion of the dendrites is $Cu_{3-x}As$.

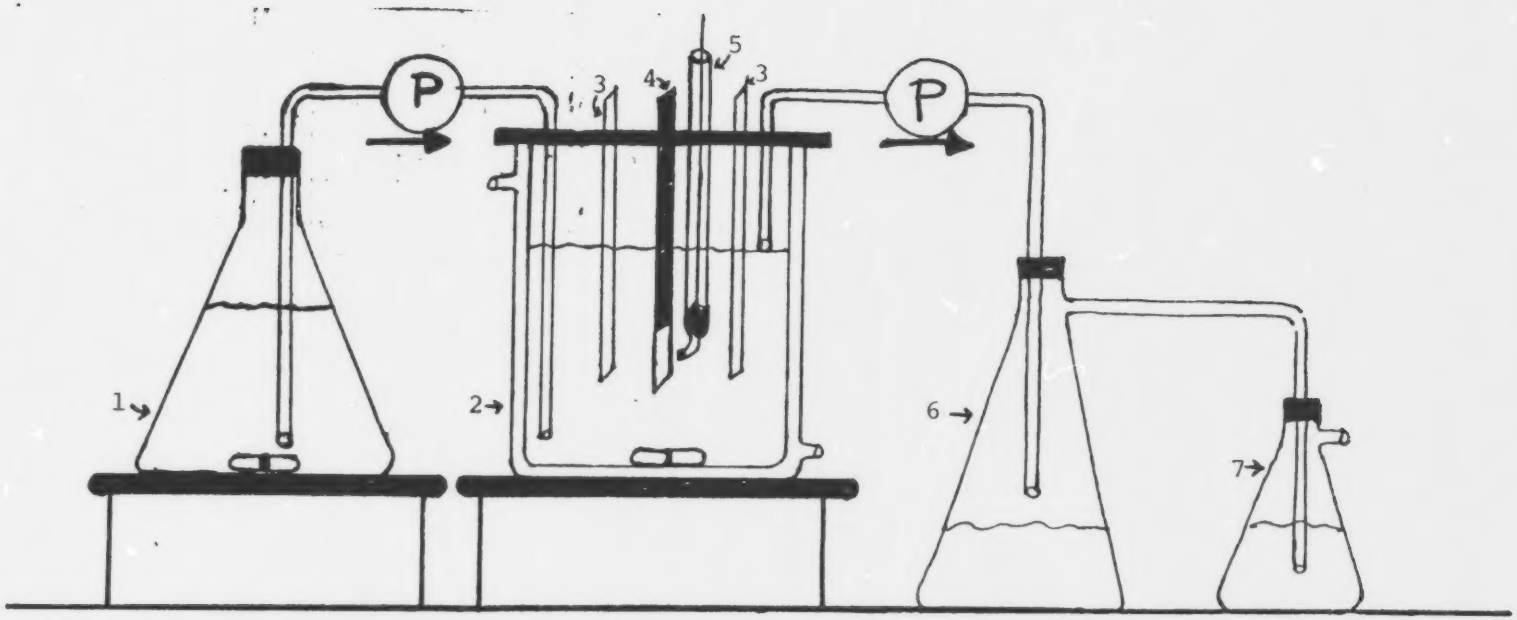
Fig. 10. - Backscattered electron micrograph taken at higher magnification than in Figure 9. The field shows the deposit of $Cu_{3-x}As$ on the copper plate and lower portions of the dendrites.

Fig. 11. - X-ray micrograph for AsKα of the area shown in Figure 10. The concentrated white dots clearly define the $Cu_{3-x}As$ phase.



1. Arsine Detector; 2. Circulation Vessel; 3. Electrowinning Cell; 4. Pb-Sb anode; 5. Ti Cathode; 6. Hg/Hg_2SO_4 Reference Electrode.

Figure 1. Experimental set-up for batch electrowinning of copper arsenide.



1. Feed Vessel; 2. Electrowinning Cell; 3. Pb-Sb anode; 4. Ti cathode; 5. Hg/Hg_2SO_4 Reference Electrode; 6. Spent Vessel; 7. Arsine Detector.

Figure 2. Experimental set-up for Continuous Feed Electrowinning of Copper Arsenide.

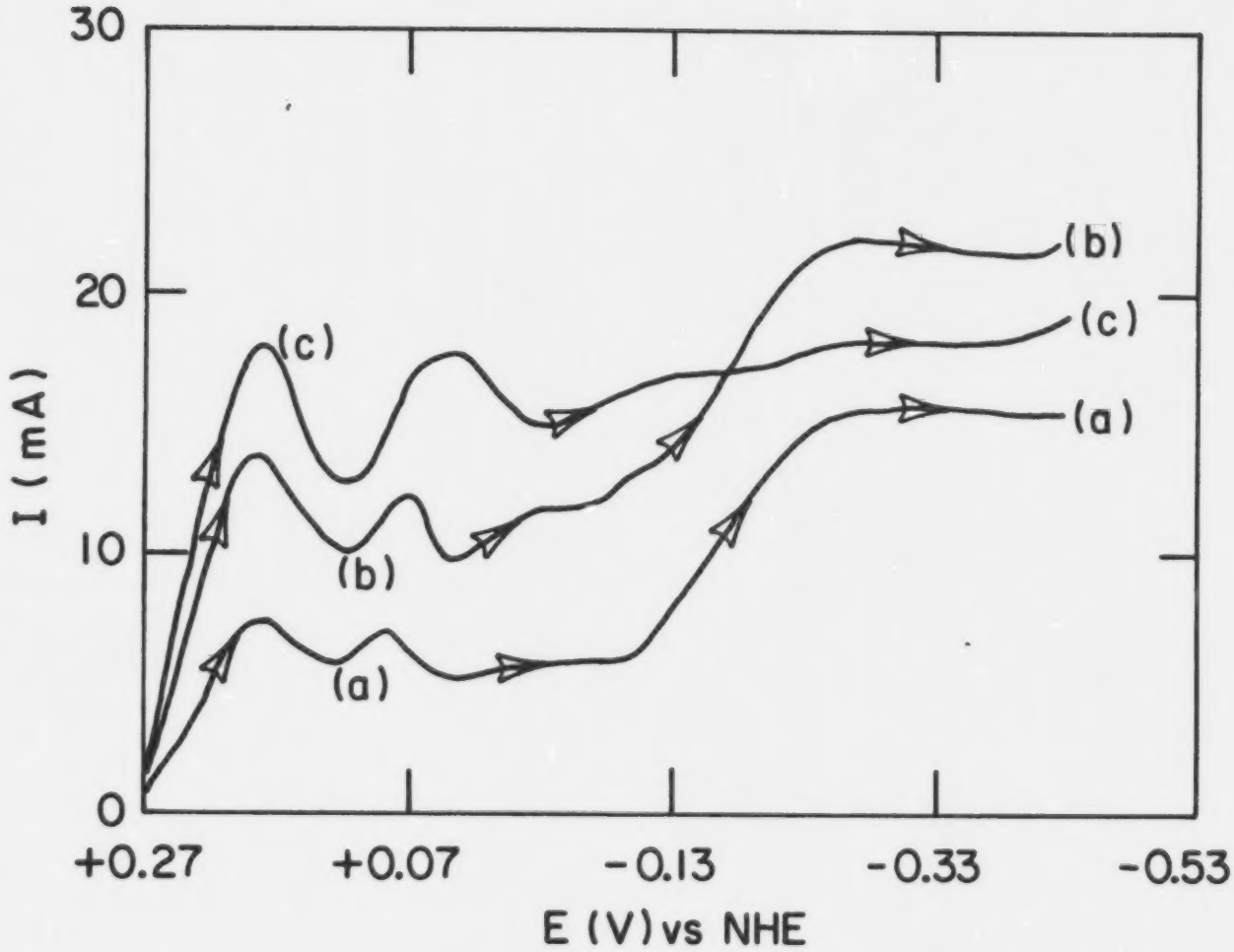


Fig. 3. Potentiodynamic i-E curves obtained for electrolytes (a), (b) and (c), Table I, at 20 mV/s and 65°C.

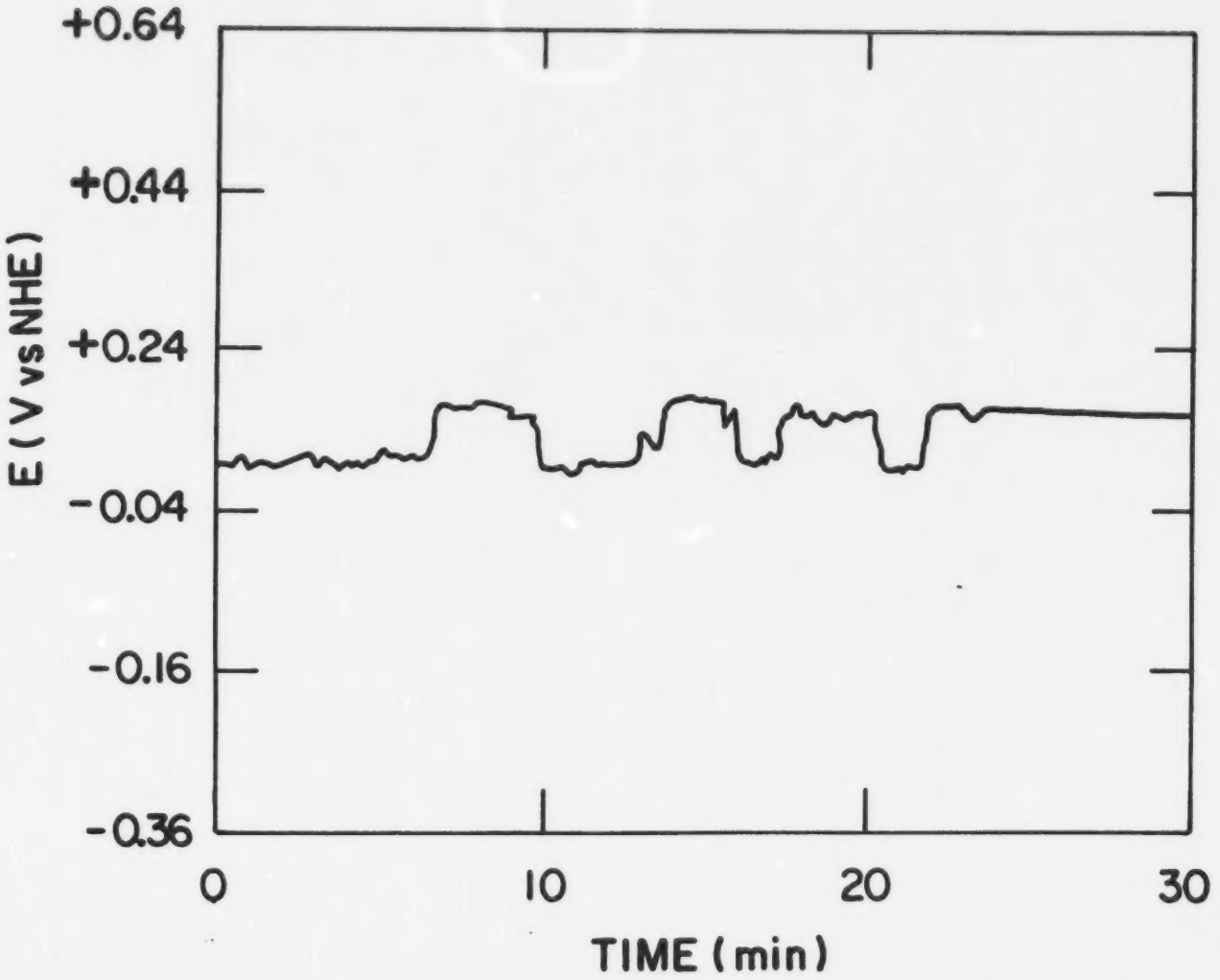


Fig. 4(a). Potential-time segments obtained at 40 A/ft^2 (430 A/m^2) for copper arsenide deposition from electrolyte (c), Table 1, at 65°C with circulation rate = 2 mL/min. 2.5 - 3.0 h segment.

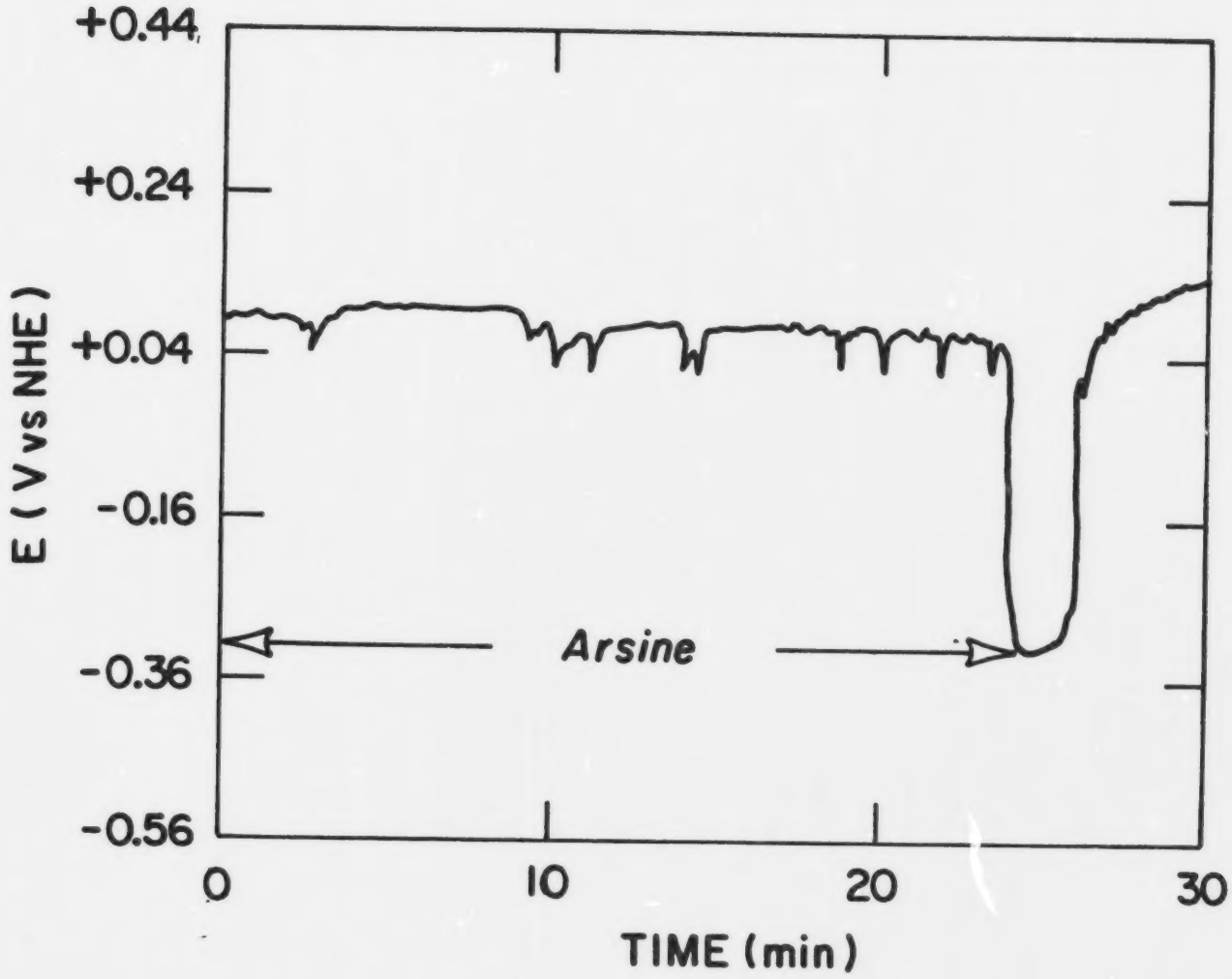


Fig 4(b). Potential-time segments obtained at 40 A/ft^2 (430 A/m^2) for copper arsenide deposition from electrolyte (c), Table I, at 65°C with circulation rate = 2 mL/min. 4.5 - 5.0 h segment.

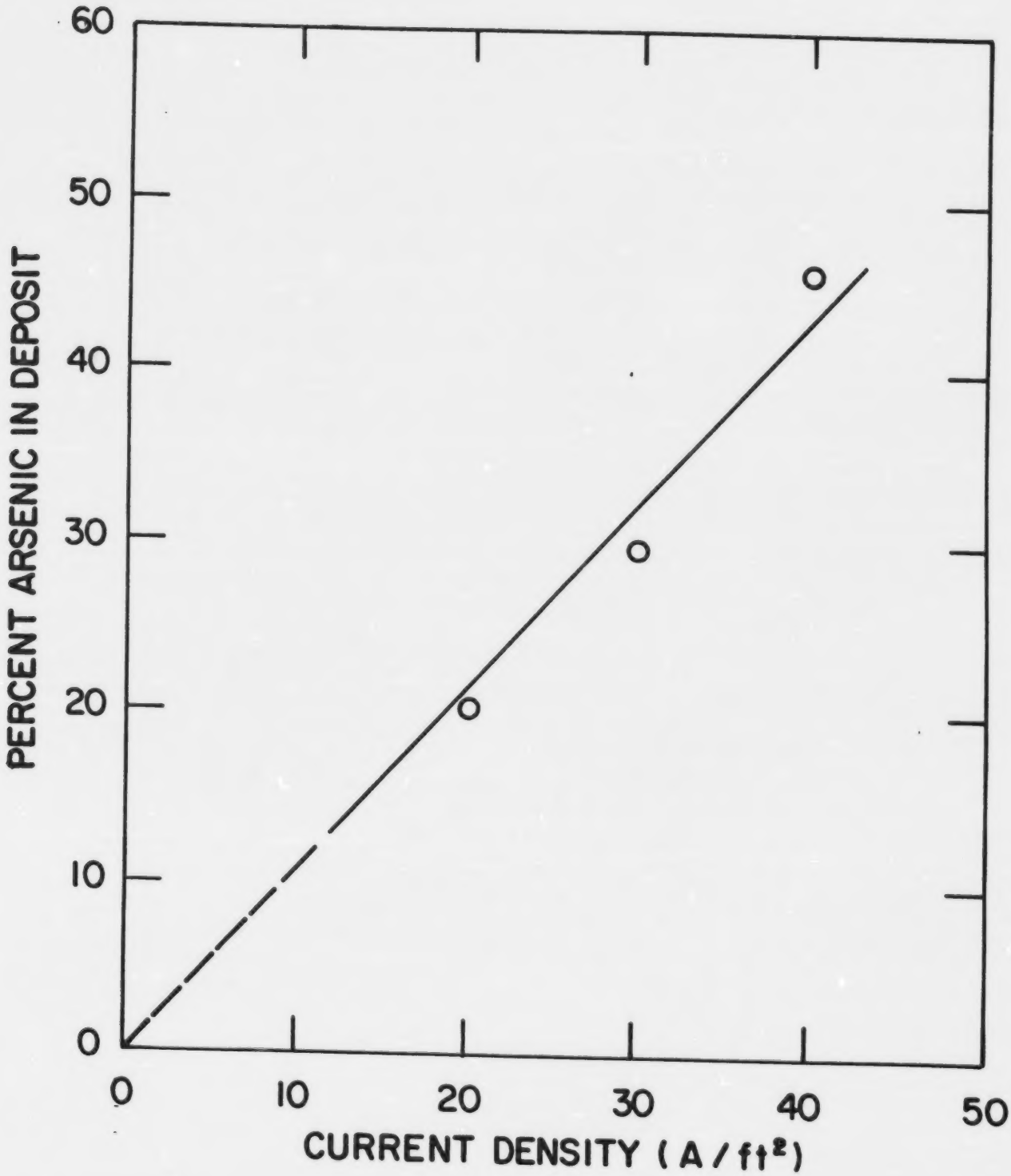


Fig. 5. Plot of percent arsenic in the deposit vs current density obtained for an initial electrolyte with Cu/As = 0.5 at 65°C and circulation rate = 2 mL/min (1 A/ft^2 = 10.76 A/m^2).

FIG. 6

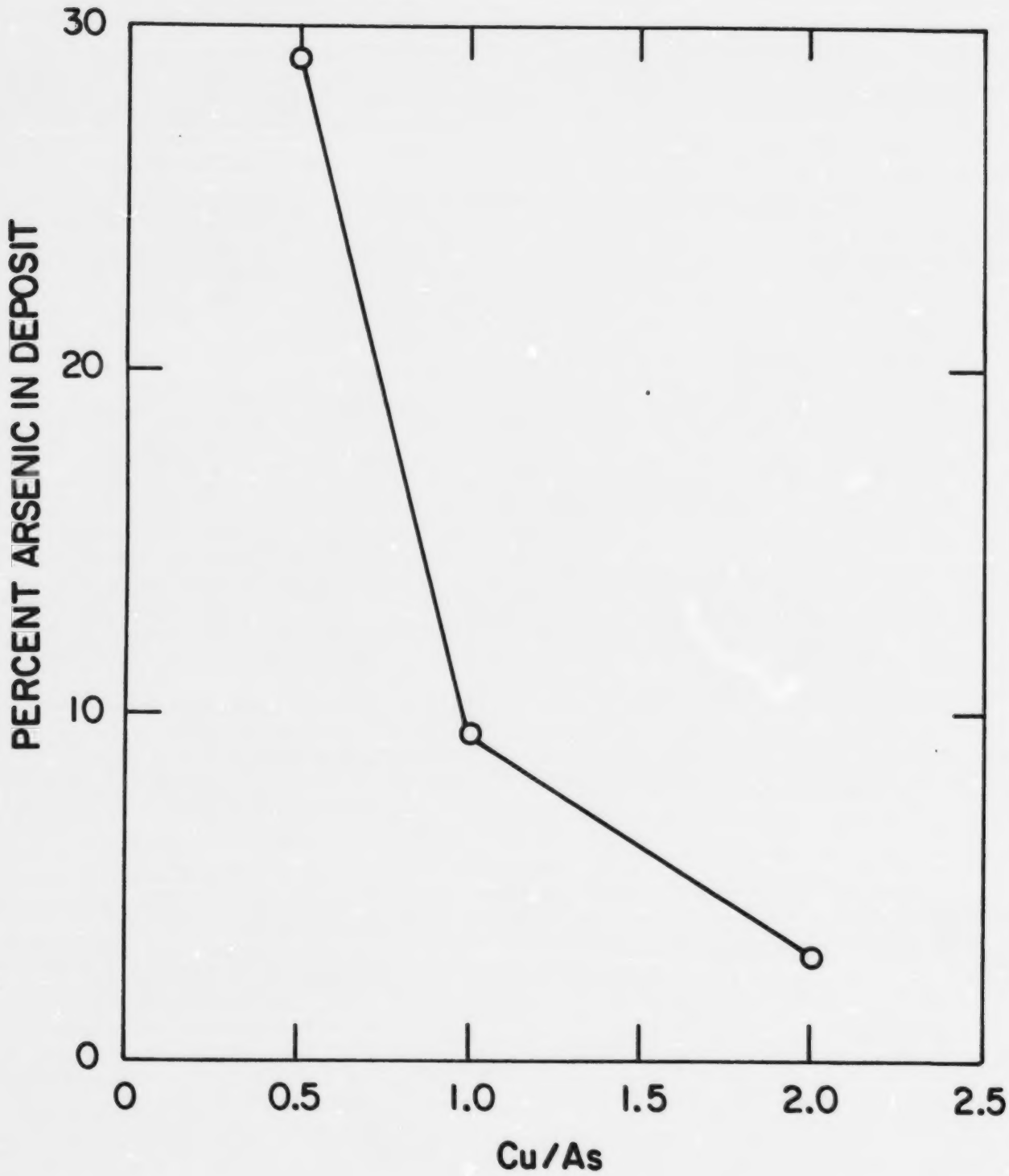


Fig. 6. Plot of percent arsenic in the deposit vs Cu/As ratio obtained at 30 A/ft^2 (323 A/m^2), 65°C and circulation rate = 2 mL/min.

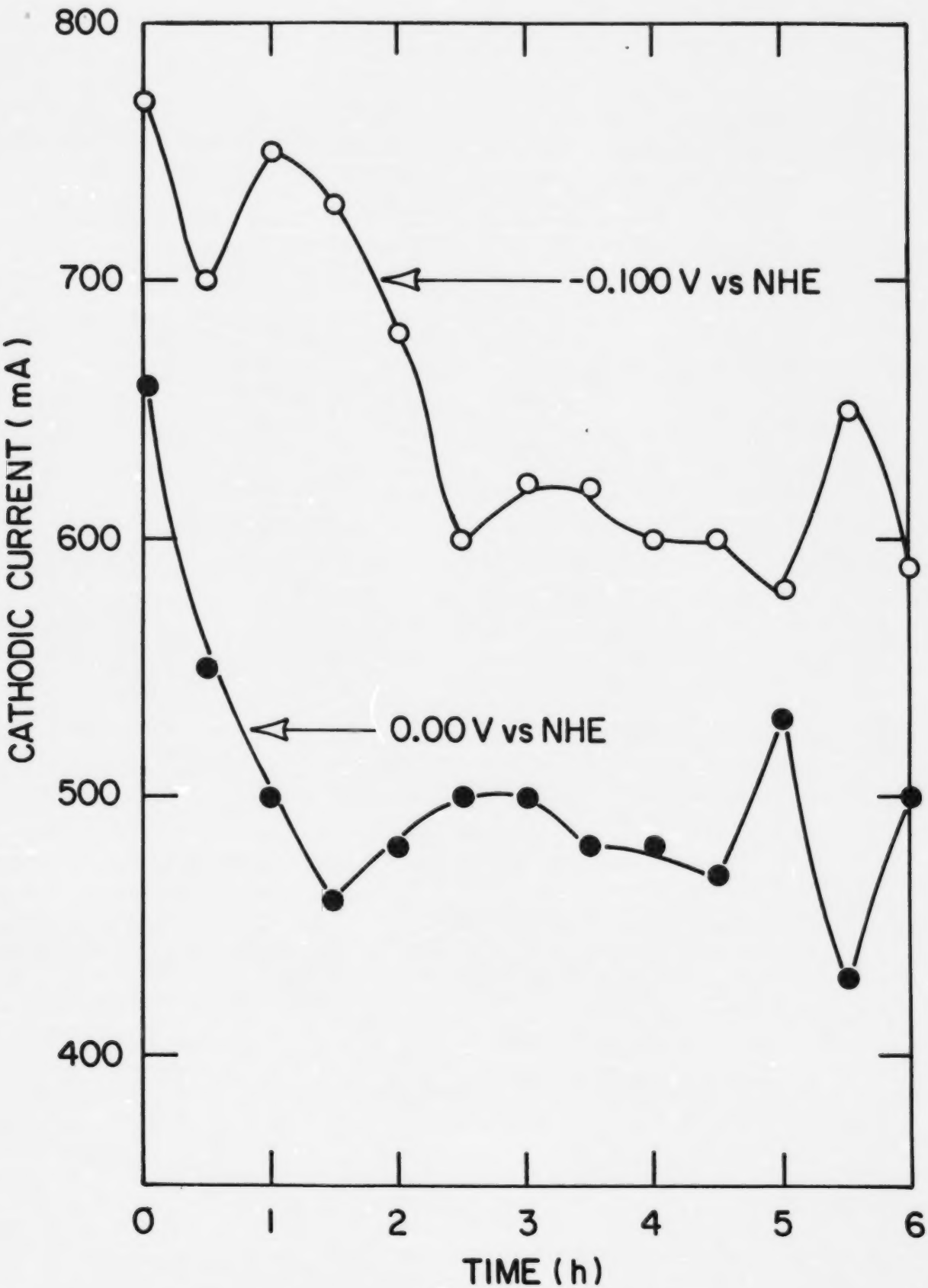


Fig. 7. Cathodic current vs time plots for copper arsenide deposition under controlled potential electrolysis.

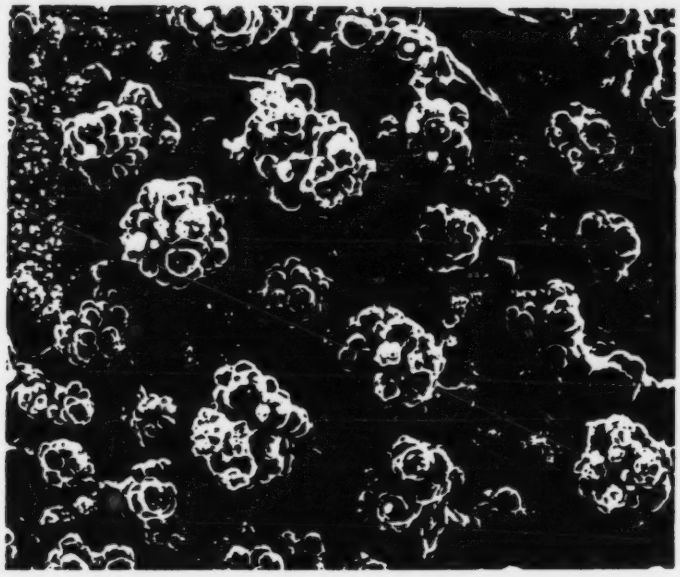


Figure 8. Scanning electron micrograph showing the surface of the copper arsenide deposit electrowon at 20 A/ft^2 (215 A/m^2).

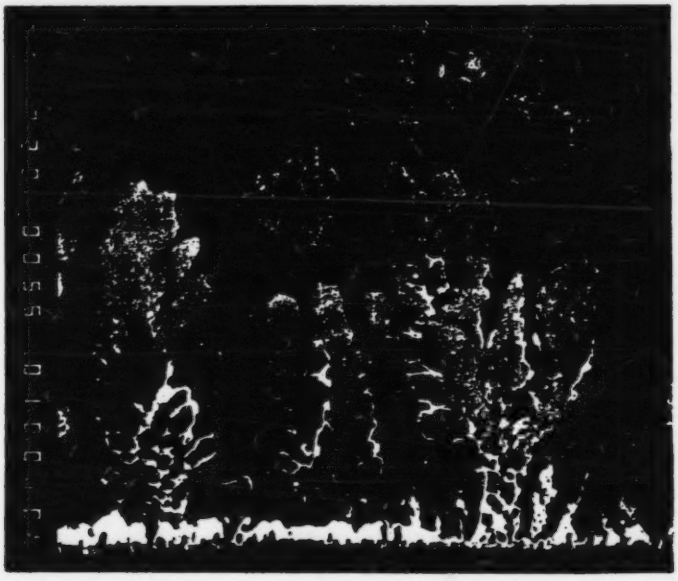


Figure 9. Backscattered electron micrograph of a polished section prepared from a copper arsenide deposit showing the height and size of the copper dendrites (medium grey). The white layer on the copper plate and thin coating on the lower portion of the dendrites is $Cu_{3-x}As$.

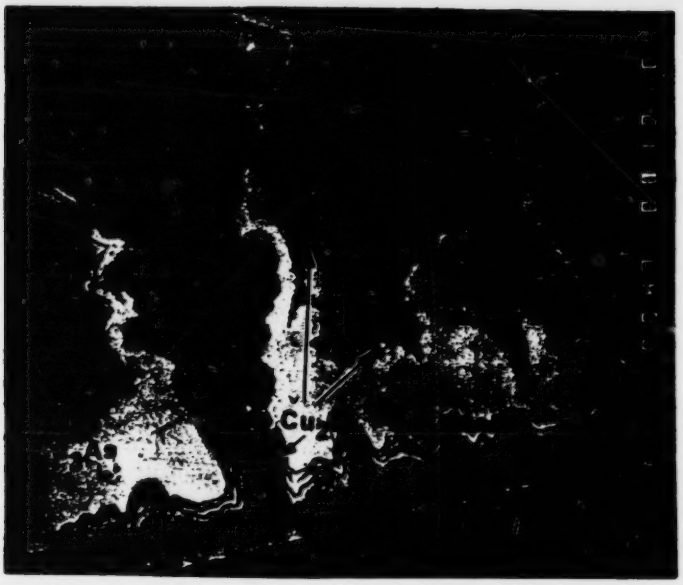


Figure 10. Backscattered electron micrograph taken at higher magnification than in Figure 9. The field shows the deposit of $Cu_{3-x}As$ on the copper plate and lower portions of the dendrites.

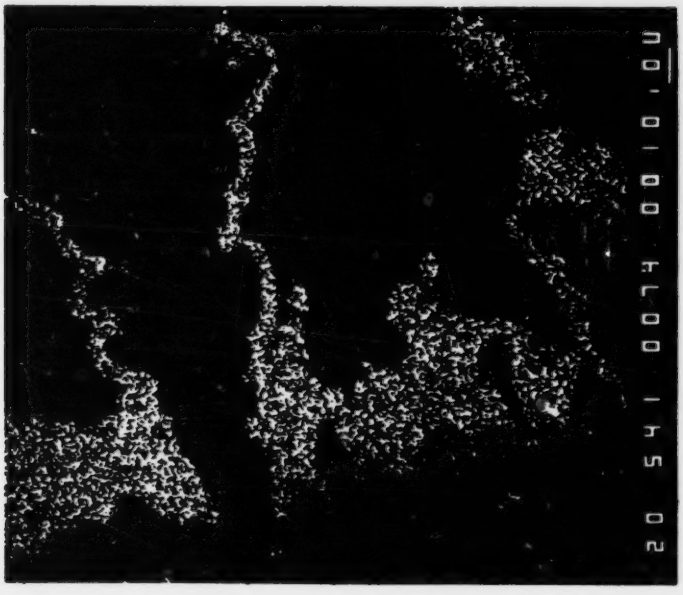


Figure 11. X-ray micrograph for AsKα of the area shown in Figure 10. The concentrated white dots clearly define the $Cu_{3-x}As$.